

Distinction of Metal Species of Phytate by Solid-State Spectroscopic Techniques

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Solid-state ^{31}P nuclear magnetic resonance (NMR) and x-ray absorption near edge structure (XANES) spectroscopies have provided knowledge on metal speciation of inorganic P. No effort has been made, however, to accurately assign speciated metal phytates (inositol hexaphosphoric acid salts) using these advanced techniques. Phytate is a predominant form of organic P in animal manure, soil, and other organic substances as each year 51 million Mg of phytate are formed in crops and fruits globally. Currently, the interactions and fate of phytate in the environment are poorly understood. Here we show the solid-state spectral characteristics of six metal phytates. Both spectra were affected by the metal species of the phytates, as significant differences were observed in the shape and position of spectra among the metal phytates. Reference spectra of these pure metal phytate compounds may help in identifying metal species of phytate in environmental samples by these advanced spectroscopic technologies.

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Abbreviations: MAS, magic angle spinning; NMR, nuclear magnetic resonance; XANES, x-ray absorption near edge structure.

IT IS EXPECTED THAT THE FIRST 50 YR of the 21st century will see rapid agricultural expansion to meet the demands of a wealthier and larger global population (Tilman et al., 2001). With this rapid expansion comes the threat of eutrophication. Simulation models predict that it could take 1000 yr or more to recover from eutrophication caused by agricultural overenrichment of soils (Carpenter, 2005). Increased basic knowledge of P dynamics is needed to minimize these deleterious impacts.

More than 35 million Mg of phytic acid (inositol hexaphosphoric acid), or 51 million Mg of phytate, are formed in crops and fruits each year globally (Lott et al., 2000). Phytate has been found to be a predominant form of organic P in animal manure, soil, and other organic substances (Cosgrove, 1962; He et al., 2006c; Herbes et al., 1975; Turner et al., 2002). Although some information is available on the basic chemistry of phytate (Turner et al., 2002), the interactions and fate of phytate in the environment remain poorly understood. There is an urgent need to better understand the behavior, mobility, and biological availability of phytate in the environment (Turner et al., 2006). Phytate contains a six-C ring with 1 H and 1 phosphate attached to each C. Each of the six phosphate groups is attached in an ester linkage and retains two replaceable Hs. These two non-ester hydroxyl groups should impart some inorganic P-like (orthophosphate bond) properties to phytate, leading to interactions of phytate with various metal ions in the environment to form various soluble or insoluble compounds (phytate salts). One of the key issues in P chemistry is metal speciation of P in the environment, as phosphate can interact with metal ions and oxides to affect the solubility and mobility of phosphates. Metal speciation of phosphate and metal-phosphate interactions can be investigated by solid-state ^{31}P NMR and XANES spectroscopic techniques (Hunger et al., 2004; Peak et al., 2002; Sato et al., 2005; Toor et al., 2005). Whereas these studies have shed light on the metal speciation of inorganic phosphate, it is not possible to resolve these spectral data in detail on specific metal-phytate species due to the lack of reference spectra. To evaluate the feasibility of metal speciation of phytates by solid-state ^{31}P NMR and XANES spectroscopic techniques, we determined and analyzed the solid-state spectral characteristics of six metal phytates. These spectra of metal phytates would provide reference spectral characteristics for identifying relevant metal species of phytate as these metals (Na, K, Ca, Mn, Al, and Fe) are abundant in soils (Sato et al., 2005; Shand et al., 1999) and animal manures (He et al., 2003, 2006c; Peak et al., 2002) and phytate is inclined to interact with them (Dao, 2003; He et al., 2006a).

MATERIALS AND METHODS

The Na and K compounds of phytates and orthophosphates were purchased from Sigma Chemical Co. (St. Louis, MO). The Ca, Mn, Al, and Fe compounds were made in-house (He et al., 2006b). All chemicals were ground to powders in an agate mortar and kept in a desiccator at room temperature until use.

Solid-state ^{31}P NMR spectra were collected on a Varian Inova 500 spectrometer (Varian Inc., Palo Alto, CA) operating at 202.489 MHz using a Doty Scientific 4mm/XC magic angle spinning (MAS) probe (Doty Scientific, Columbia, SC). Bloch decays of 50 ms were collected with a 200 ppm window after 30° excitation pulses. A relaxation delay

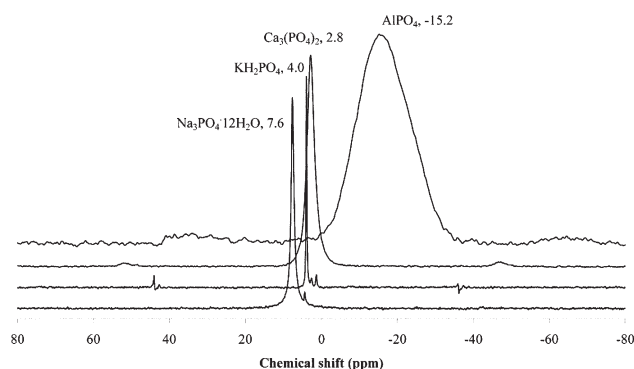


Fig. 1. Solid-state ^{31}P spectra of metal inorganic phosphates. The values following the compound names are isotropic chemical shifts (in ppm).

of 1 s was used between each transient. Two-pulse phase modulated proton dipolar decoupling with a field strength of 45 kHz was applied during acquisition. A MAS speed of 10 kHz was used, and between 8 and 64 scans were collected for most runs.

Phosphorus K-edge XANES spectra were collected at beam line X19A of the National Synchrotron Light Source at Brookhaven National Laboratory in Upton, NY (Caliebe et al., 2004; Yang et al., 1990). The beam line consists of a Si(111) monochromator and collimating and focusing mirrors. The energy resolution of the monochromator at the P K-edge at 2.1 keV is about 0.4 eV. The intensity of the x-ray beam was measured by a He-purged ion chamber, and it is about 2×10^{10} Hz. The sample was mounted in a He-purged sample cell together with the detector. We used a brush to apply finely ground powder on cellophane tape, which does not contain any P. This was confirmed by measuring the P K-edge XANES of clean cellophane tape. Data were collected in fluorescence yield mode with a PIPS detector (Canberra, Meriden, CT). We also measured the same samples in total electron yield mode with an electron yield detector (a Lytle detector). We applied a rather high voltage of 300 V on the grid to eliminate charging effects of the samples. The data are background corrected (between -40 and -20 eV), and normalized to an edge-step of 1 between 40 and 100 eV. The main purpose of these experiments was to show that the XANES of different metal phytate compounds is visible in the XANES; therefore, the spectra were reference scans of the individual pure compounds and there were no scans of mixed compounds or soil or manure samples.

RESULTS AND DISCUSSION

Manganese and Fe phosphates and phytates were not detectable by solid-state ^{31}P NMR analysis due to the paramagnetic line broadening. In solid-state ^{31}P NMR spectra (Fig. 1), Na, Ca, and Al phosphates, as well as acidic K phosphate, possessed distinguishable major isotropic chemical shift bands. The chemical shifts of $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, KH_2PO_4 , and $\text{Ca}_3(\text{PO}_4)_2$ were close to those reported in literature (Table 1; Turner et al., 1986). The chemical shift (-15.2 ppm) of our in-house synthesized AlPO_4 was higher than that (-24.5 ppm) in the same literature; however, it fell well in the range of -7 to -25 ppm of AlPO_4 species reported by different researchers (McDowell et al., 2002). Unlike AlPO_4 , the chemical shift (2.8 ppm) of our in-house synthesized Ca phosphate was identical to that of hydroxyapatite (Ca tribasic phosphate with some Ca hydroxide) (Rothwell et al., 1980). In fact, the chemical shifts of all Ca hydroxyapatites with different Ca/P ratios (i.e., Ca tribasic phosphate with different amounts of Ca hydroxide)

Table 1. Solid state ^{31}P nuclear magnetic resonance spectral features of metal phytate and inorganic phosphate compounds.

Chemical	Major peak	Spin sideband	Reference
	ppm		
$\text{Na}_{12}\text{IP6}$	7.5	68.2, -41.7	This work
$\text{Na}_{12}\text{IP6}$	7.6	—	Shand et al. (1999)
Na-IP6†	3.6	—	Hunger et al. (2004)
$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	7.6	Not apparent	This work
$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	7.8	—	Turner et al. (1986)
$\text{K}_2\text{H}_{10}\text{IP6}$	-0.7	48.6, -49.8	This work
KH_2PO_4	4.0	Not apparent	This work
KH_2PO_4	4.3	—	Turner et al. (1986)
$\text{Ca}_6\text{IP6}$	0.5	49.8, -48.8	This work
Ca-IP6†	-2.1	—	Hunger et al. (2004)
$\text{Ca}_3(\text{PO}_4)_2$	2.8	Not apparent	This work
$\text{Ca}_3(\text{PO}_4)_2$	3.0	—	Turner et al. (1986)
$\text{Ca}_{10}(\text{H}_2\text{O})_2(\text{PO}_4)_6$	2.8	Not apparent	Rothwell et al. (1980)
$\text{Al}_4\text{IP6}$	-14.8	36.6, -63.0	This work
AlPO_4	-15.2	Not apparent	This work
AlPO_4	-24.5	—	Turner et al. (1986)
$\text{AlPO}_4 \cdot n\text{H}_2\text{O}$	-25 to -7	—	McDowell et al. (2002)

† Ratio of metal to IP6 was not specified.

‡ Information was not reported.

were 2.8 ppm (Rothwell et al., 1980). On the other hand, the chemical shift does change with protonated (acidic) Ca phosphates (Rothwell et al., 1980). Therefore, the chemical shift at 2.8 ppm seems valuable in identifying Ca tribasic phosphate.

The four metal phytates possessed different major chemical shift bands (Fig. 2). Like their inorganic P counterparts, the chemical shifts of metal phytates were sensitive to the cation charge. The value (7.5 ppm) of $\text{Na}_{12}\text{IP6}$ in this work was the same (7.6 ppm) as that reported previously (Shand et al., 1999). Hunger et al. (2004) reported the chemical shift values of 3.6 and -2.1 ppm for Na and Ca phytate, respectively (Table 1); however, the stoichiometry of metal vs. phytate was not reported. Using solid-state ^{31}P NMR spectroscopy, P speciation in peat and mineral soils (Shand et al., 1999), dairy manures (Jayasundera et al., 2005), and $\text{Al}_2(\text{SO}_4)_3$ -amended and unamended poultry litter (Hunger et al., 2004) have been explored. Apparently due to no appropriate compounds available, these researchers only used commercially available Na and Ca phytate ($\text{CaH}_{10}\text{IP6}$) to obtain reference spectra of phytate compounds without consideration of the

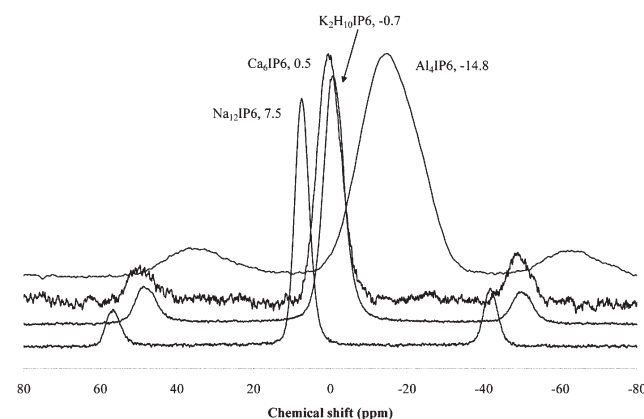


Fig. 2. Solid-state ^{31}P spectra of metal phytates (IP6). The values following the compound names are isotropic chemical shifts (in ppm). The symmetric minor peaks are spinning side bands.

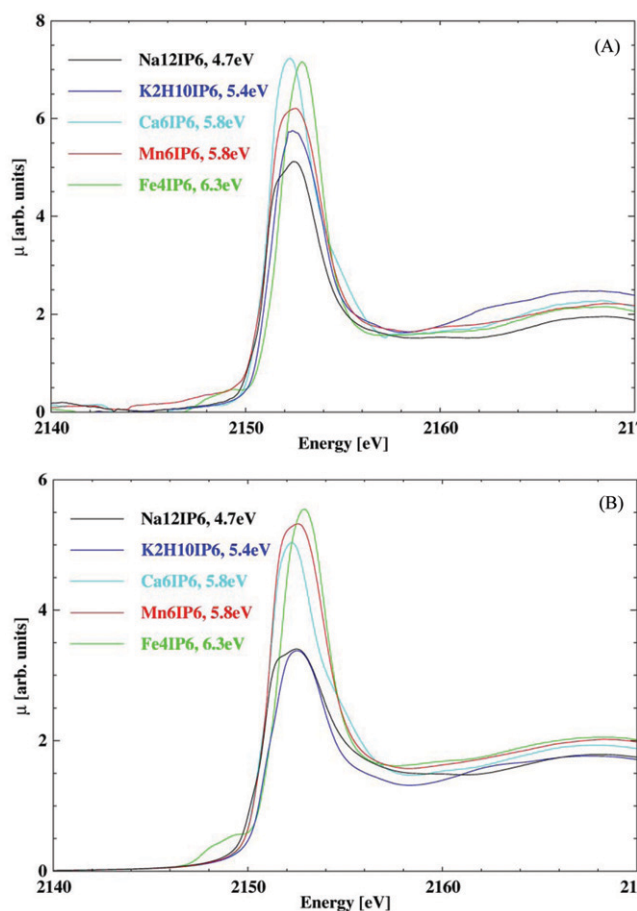


Fig. 3. Phosphorus K-edge XANES spectra of metal phytate compounds. The values following the compound names are the edge shift (in eV) relative to the nominal P-K-edge at 2145.5 eV: (A) data were collected with total electron yield mode; (B) data were collected with total fluorescence yield mode.

effects of the metal ions. We hope our work will promote the awareness of the impacts of metal counterparts on the solid-state ^{31}P NMR spectral features of phytate.

In addition to the change in chemical shifts, the spectra of metal phytates demonstrated strong spinning side bands. These characteristic spinning side bands were apparently associated with the presence of six

phosphate groups bound together by a six-member C ring. These spinning side bands may be used to distinguish phytate species from their corresponding inorganic phosphate species, especially when their major bands are similar, such as is the case between dodecasodium phytate and trisodium phosphate, and between tetraaluminum phytate and aluminum phosphate (Table 1). Spinning side band features have been used to characterize solid Ca phosphate phases (Rothwell et al., 1980). For example, apatite has less intense spinning side bands than protonated Ca-P at slow MAS speeds (1–4 kHz; Rothwell et al., 1980). Our research indicates that, with appropriate reference metal phytates, solid-state ^{31}P NMR spectroscopy has the ability to differentiate some metal species of phytates, although external factors can influence the line width of both major and sideband peaks.

The main difference in the measurements of XANES spectral data with electron yield and fluorescence yield modes was the intensity of the white line, which was suppressed in fluorescence yield mode (Fig. 3). Whereas the data collected in the electron yield measurements were more surface sensitive and did not suffer from self-absorption effects, all electron yield measurements were quite noisy. On the other hand, XANES spectral data collected in fluorescence mode showed some self-absorption effects, but the position and splitting of peaks were well reproduced, as well as the trend of intensity ratios of the white lines. Furthermore, the data measured in fluorescence mode were less noisy. Significant differences can be observed in the intensity, position, and width of the white line at approximately 2153 eV. Since all phytate groups have identical bonds, the white lines for each individual phytate are not split. Different metal ions, however, slightly change the white line energy positions. The white line energy positions were in the order of $\text{Na} < \text{K} < \text{Ca} < \text{Mn} < \text{Fe}$ phytates. The change was in the same order as observed with metal phosphate compounds, although the exact positions were different (Franke and Hormes, 1995; Okude et al., 1999). Both phytates with a monovalent metal ion, $\text{Na}_{12}\text{IP}_6$ and $\text{K}_2\text{H}_{10}\text{IP}_6$, have a fairly weak white line compared with the divalent and trivalent metal-ion phytates. Furthermore, there is a subtle difference between the two monovalent phytates. The spectrum of $\text{Na}_{12}\text{IP}_6$ has a fairly broad peak with a shoulder, while that of $\text{K}_2\text{H}_{10}\text{IP}_6$ shows just one peak. In addition, a little pre-edge feature was present in the spectrum of Fe phytate, which was also observed in the spectra of Fe-relevant inorganic phosphates (Franke and Hormes, 1995; Khare et al., 2004). If confirmed, this feature could be especially useful for identifying Fe P species, considering that the solid-state ^{31}P NMR spectroscopy was not able to identify it due to the paramagnetic property of Fe. In summary, our observations contradict two previous reports that

XANES spectra of phytates are featureless (Beauchemin et al., 2003; Peak et al., 2002). The use of a single phytate as a reference compound by others (Beauchemin et al., 2003; Peak et al., 2002; Table 2) may have mainly influenced their observations although the sample conditions (moist pastes; Peak et al., 2002) could also have some impacts.

Similar to solid-state ^{31}P NMR and XANES spectral observations, the major P–O bond peaks in Fourier-transform infrared spectra (FT-IR) of these compounds are also broadened or split (He et al., 2006b). Although the principles of the three spectroscopies are different, their spectral features are relevant to the molecular structures and compositions of detected samples. Compared with sharp bands in their inorganic phosphate counterparts, the broadened or split spectral bands with all three methods indicated that this phenomenon was not due to abnormal or erroneous observations, but to the intrinsic molecular

Table 2. Phosphorus K-edge XANES white line peaks of phytate compounds collected by total electron yield mode (EY) or total fluorescence yield mode (FY) (relative to the nominal P K-edge at 2149.5 eV).

Chemical	Major peak eV	Mode for data collection	Reference
$\text{Na}_{12}\text{IP}_6$	2.3	EY and FY	This work
$\text{K}_2\text{H}_{10}\text{IP}_6$	3.0	EY and FY	This work
Ca_6IP_6	2.8	EY and FY	This work
Ca-IP_6^\dagger	9.0 \ddagger	FY	Peak et al. (2002)
Ca-IP_6 (aqueous) \dagger	9.0 \ddagger	FY	Peak et al. (2002)
Mn_6IP_6	3.1	EY and FY	This work
Fe_4IP_6	3.4	EY and FY	This work
IP_6^\S	1.5 \ddagger	FY	Beauchemin et al. (2003)
IP_6^\S	8.5 \ddagger	EY and FY	Toor et al. (2005)
IP_6^\S	−0.5 \ddagger	EY and FY	Lombi et al. (2006)

\dagger Ratio of metal to IP6 was not specified.

\ddagger Estimated based on the information in the cited reference.

\S Cation species (metal or H) was not clearly specified

structures of phytate compounds. The six-C ring of phytate apparently constrains the six phosphate groups of phytate to certain specific stereoisomeric positions. In other words, there are structurally different COPO₃ (or C–O bonds and P–O bonds) in each phytate molecule, whereas there is only a single uniform PO₄ group in inorganic metal phosphate. These structurally different COPO₃ groups would yield minor differences in the bond vibrations, magnetic resonance of their nuclei, and the electron environment, thus producing the unique broad or split peak features of phytate in FT-IR, NMR, and XANES spectra, respectively. More investigation of the phenomena would help in elucidating the molecular structure of these metal phytates and in identifying the metal phytates in the environmental samples with these unique features.

CONCLUSIONS

Metal speciation of inorganic phosphate and metal–phosphate interactions have been investigated by solid-state ³¹P NMR and XANES spectroscopic techniques. In this study, we obtained and analyzed solid-state ³¹P NMR or XANES, or both, spectral features of Na, Ca, Mn, Al, and Fe phytates, as well as acidic K phytate. Both spectra were affected by the metal species of the phytates. The chemical shift values in solid-state ³¹P NMR spectra decreased with increasing metal ion valence. Compared with inorganic phosphates, the solid-state ³¹P NMR spectra of metal phytates demonstrated strong spinning side bands. Similarly, differences were observed among the P K-edge XANES spectra of five metal phytate compounds. Significant differences were observed in the intensity, position, and width of the white line at approximately 2153 eV. This study demonstrated that the solid-state spectral features of different metal phytate compounds were visible in both ³¹P NMR and P K-edge XANES. Establishing reference spectra using multiple pure metal phytate compounds, which are not available in literature, may help in identifying metal species of phytate in environmental samples, which were not investigated in this study, by these advanced spectroscopic technologies.

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